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TREATMENT OF WASTEWATER FROM THE FOUNDRY INDUSTRY USING FENTON PROCESS

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Abstract

The aim of the study was to evaluate the effectiveness of the Fenton process in the treatment of selected wastewater from the foundry industry, which was initially coagulated. In the coagulation process, contaminants found in the suspended and colloidal phase were separated from the wastewater. The selection of the favorable course of the Fenton process was carried out with the following parameters in mind: wastewater pH, hydrogen peroxide dose, Fe^{2+}/H_2O_2 mass ratio and process time. The selected parameters of the Fenton process were: wastewater pH 2.5, hydrogen peroxide dose 5.00 g/L, Fe^{2+}/H_2O_2 mass ratio 0.3 and process time 120 min. For the given parameters, high efficiency of the Fenton process in lowering the chemical oxygen demand (COD) of the treated wastewater from the foundry industry was demonstrated. In wastewater, the concentration of non-ionic surfactants (NS) also decreased.

Keywords: **Foundry industry; Wastewater treatment; Fenton process.**

1. INTRODUCTION

The increase in automation and intensification of production processes and the reduction of the amount of water used in these processes leads to a significant increase of pollutants in industrial wastewater. Bearing in mind the progressive degradation of the natural environment, there is a need to limit the negative impact of industry on various elements of the environment, including on surface waters through the use of effective methods of wastewater treatment. This situation applies to various industries, including the foundry industry.

Important environmental aspects of the non-ferrous metal foundry industry include the emission of organic pollutants from pyrolysis and thermal decomposition of binders, protective coatings, etc. (including phenol, formaldehyde, amines, hydrogen cyanide, polycyclic aromatic hydrocarbons – PAHs, benzene, and Volatile Organic Compounds – VOC), as well as the generation of wastewater, e.g. from wet dedusting, and – in the case of pressure casting – transport of hydraulic fluids or coolant to the water circuit in an industrial plant. Significant amounts of rinse water are also generated, used baths containing high levels of resins, as well as wastewater from technological equipment containing worked hydraulic fluids, coolants, release agents and lubricants for casting moulds [1, 2]. The composition of many preparations used in production processes is subject to patent protection of the manufacturer, which is why it is often difficult to determine the exact qualitative composition of the wastewater flowing into the treatment plant when it contains preparations mentioned above.

Industrial wastewater treatment is based on biological, physical, chemical and physicochemical methods. The use of individual methods or their configuration depends on the qualitative and quantitative characteristics of the supplied wastewater and the technical and economic capabilities of the unit dealing with their treatment. Due to the diverse composition of wastewater and their high variability in time, it is often necessary to use several methods. Conventional methods, which are simple to implement and economically efficient, such as straining, sedimentation, flotation, precipitation or coagulation, are not as efficient and allow only for the transfer of pollutants from the liquid phase (wastewater) to another, e.g. solid (deposits). They are often characterized by low efficiency in reducing the concentration of dissolved organic pollutants, in the case of which the use of biological methods is not possible due to the coexistence of a large amount of non-biodegradable or toxic fractions. The solution to the above-mentioned disadvantages may be the inclusion of alternative methods in the wastewater treatment plant line, such as advanced oxidation processes (AOPs). These methods, as a result of the generation of OH• highly reactive hydroxyl radicals, which react with almost all organic substances, allow for their degradation, also in the case of toxic and biodegradable-resistant pollutants. The hydroxyl radical undergoes chemical reactions with almost all organic pollutants, as well as with many inorganic substances, without producing harmful by-products [3–10].

One of the most common and effective methods for producing hydroxyl radicals is a mixture of hydrogen peroxide (H_2O_2) and iron salts (II), i.e. Fenton's reagent [11]. An additional advantage of the Fenton process is the simultaneous removal of pollutants contained in the treated solution by means of coagulation, caused by the presence of Fe^{3+} and precipitation (OH^-+ Fe^{3+}) [4, 7, 12].

The classic Fenton process is the subject of many studies on the possibility of using it to eliminate individual organic substances, as well as to treat real wastewater from various industries. For example, in [13] research was conducted on the treatment of effluent collected from the municipal waste landfill in Kozodrza near Rzeszów that was subjected to reverse osmosis. This effluent had a pH of 7.5 and COD at the level of approx. 7500 mg/L. The wastewater pH was not corrected in these tests. The highest level of COD reduction was obtained using the Fe^{2+}/H_2O_2 of 0.07 (approx. 85%). In turn, research on the use of Fenton's reagent for the treatment of concentrated wastewater from the production of maleic anhydride presented in [14] showed approx. 91% reduction of wastewater COD with the following parameters: (pH = 3.0, Fe^{2+}/H_2O_2 = 0.33, process time 120 min, 5% CaO solution to pH 7.0). Fenton's reaction has also found its application in the treatment of wastewater from the textile industry [15]. Studies have documented the effect of color removal exceeding 97%, as well as a significant reduction in COD (approx. 90%) for wastewater containing five types of dyes (suspension, acid, basic, direct and reactive) that are most commonly used in the textile industry. The selection of appropriate parameters of the Fenton reaction also allows for a significant reduction in the concentration of surfactants in the solution [16]. For example, for reaction parameters of 60 mg H_2O_2/L, 90 mg $FeSO_4$/L, pH 3 and 50 min of process time, over 95% reduction in the concentration of two anionic surfactants – alkylbenzene sulfonate (ABS) and linear alkylbenzene sulfonate (LAS) – was achieved.

The aim of the research undertaken as part of this work was to assess the possibility of using the classic Fenton reaction in the treatment of real wastewater from the foundry industry, after their initial pretreatment in the coagulation process.

2. MATERIALS AND METHODS

Characteristics of wastewater

The research was carried out using real post-production wastewater from the foundry industry. This wastewater was pre-treated to remove pollutants from the colloidal and suspended phase by using a coagulation and sedimentation process, which is described in detail in [17]. The physicochemical characteristics of the wastewater are presented in Table 1. Wastewater pre-treated in this way was characterized by a total suspension concentration of approx. 57 mg/L, COD of approx. 4045 mgO_2/L, nonionic surfactants (NS) 245 mg/L and chlorides and sulphates (VI) 70 mg/L and 51 mg/L, respectively. The concentrations of selected heavy metals in the wastewater, such as copper, zinc and nickel were also determined. However, their concentrations were below the maximum allowable threshold specified for wastewater discharged into the wastewater system of the local Water and Wastewater Company.

A CyberScan pH 1500 laboratory meter manufactured by Eutech Instruments was used to measure wastewater pH. The total suspension was determined by a weight method using a MA 110 moisture analyzer.X2.A (Radwag company). COD and NSPC were determined by spectrophotometry using the

Spectroquant® Prove 300 spectrophotometer (Merck). Determination of heavy metal concentration was carried out using the method of flame atomic absorption spectrometry (FAAS) or atomic absorption spectrometry with electrothermal atomization (ET AAS) using a contrAA® 700 apparatus from Analytik Jena AG. For the determination of anions, the ion chromatography method (DionexTM ICS-1100 from Thermo ScientificTM) was used.

Table 1.
The physico-chemical characteristics of wastewater

Parameter	Unit	Value
pH	-	6.0
Total suspended solids (TSS)	mg/L	57
Chemical oxygen demand (COD)	mgO_2/L	4045
Non-ionic surfactants (NS)	mg/L	245
Cu	mg/L	<0.05
Zn	mg/L	0.10
Ni	mg/L	<0.1
Cl-	mg/L	70
SO_4^{2-}	mg/L	51

Fenton process

The selection of optimal conditions for conducting the Fenton process was carried out using a sample of wastewater at 20°C without the addition of used baths in accordance with the following methodology:

1) acidification of wastewater to a specific pH value with a 35% H_2SO_4 solution,
2) dosing specified doses of a 35% H_2O_2 solution, as well as a PIX-100 (20% $FeCl_2$ solution) to the wastewater,
3) conducting Fenton's reaction at the prescribed time,
4) alkalization of wastewater to pH 9.0 using a 5% $Ca(OH)_2$ solution to stop the Fenton reaction and iron precipitation in the form of $Fe(OH)_3\downarrow$,
5) dosing flocculant Praestol 2515 (0.1% solution) in a dose of 4 g/L to improve the sedimentation properties of the precipitated sludge,
6) sedimentation – 1 h.

The effectiveness of the process was controlled by measuring the COD of the obtained decant.

The selection of process conditions for Fenton reactions involved the following parameters:

stage I – process pH (the range from 2.0–4.0 was tested),

stage II – H_2O_2 dose (range from 4.00-5.75 g/L),

stage III – Fe^{2+}/H_2O_2 mass ratio (range up to 0.1–0.5),

stage IV – reaction time (range from 45 to 180 min).

The presented results are the arithmetic average of the four replicates of each experiment. For all the cases assigned error (estimated based on the standard deviation) did not exceed 5% so the results are presented without marking of the ranges of error.

3. RESULTS AND DISCUSSTION

The selection of process conditions of the Fenton process was carried out using a sample of coagulated wastewater, without the addition of used baths. Firstly, for doses of H_2O_2 of 1 or 5 g/L of hydrogen dioxide, 120 min of process time and constant Fe^{2+}/H_2O_2 mass ratio of 0.3, the reaction pH was selected by testing the pH range from 2.0 to 4.0. After stopping the Fenton reaction and sedimentation of the resulting sediments, COD analysis was performed in the resulting decantates, because this parameter was taken as a measure of process efficiency. The results of these analyses are shown in Figure 1.

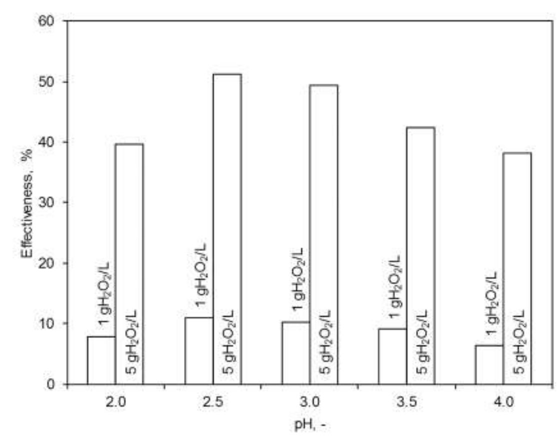

Figure 1.
Impact of wastewater pH and H_2O_2 dosage on effectiveness of decrease of COD

The highest efficiency of COD reduction for each of the applied hydrogen peroxide doses was obtained at the initial acidification of wastewater to pH 2.5. However, the effectiveness of the process clearly depended on the H_2O_2 dose. After H_2O_2 1 g/L dose, COD value decreased by approx. 11% and after a dose of 5 g/L by approx. 51%.

Subsequently, the dose of hydrogen dioxide was selected. The tests were carried out using a wastewater pH selected on the basis of the results from stage I, i.e. pH of 2.5. The dose of H_2O_2 was selected using the most effective dose from Stage I, i.e. 5 g/L and 4 lower doses (4.00, 4.25, 4.50 and 4.75 g/L) and 3 higher (5.25, 5.50, 5.75 g/L). The process time was 120 min and the mass ratio Fe^{2+}/H_2O_2 was 0.3. The test results are shown in Figure 2.

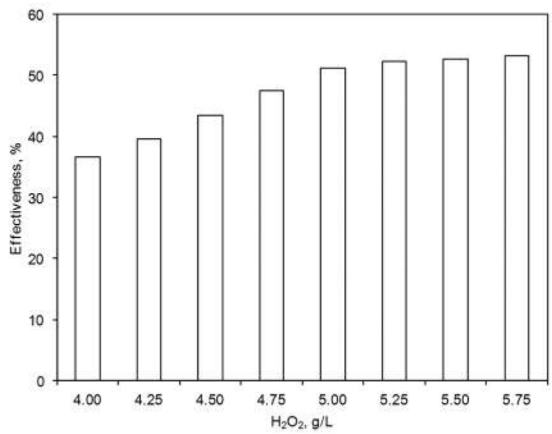

Figure 2.
Impact of H_2O_2 dosage on effectiveness of decrease of COD

The highest increase rate in process efficiency was recorded in the H_2O_2 dose range from 4.00 to 5.00 g/L. The dose of H_2O_2 5.00 g/L allowed to obtain approx. 51% reduction in COD, which was already determined in stage I. The use of higher doses of H_2O_2 resulted in a further increase in the effectiveness of COD reduction, but with a lower intensity. The application of H_2O_2 dose of 5.75 g/L allowed for the reduction of COD by approx. 53%. Comparing this result with the one obtained for the dose of 5.00 g/L, it can be concluded that increasing the dose above this value is not justified. Therefore, the best dose was H_2O_2 5.00 g/L.

The selection of Fe^{2+}/H_2O_2 mass ratio was determined using the reaction pH selected in Stage I, i.e. pH 2.5, and the dose of H_2O_2 selected in Stage II, i.e. 5.00 g of H_2O_2/L. For the process parameters listed above, Fe^{2+}/H_2O_2 mass values of 0.1, 0.2, 0.3, 0.4 and 0.5 were used. The process time was 120 min. The results are shown in Figure 3.

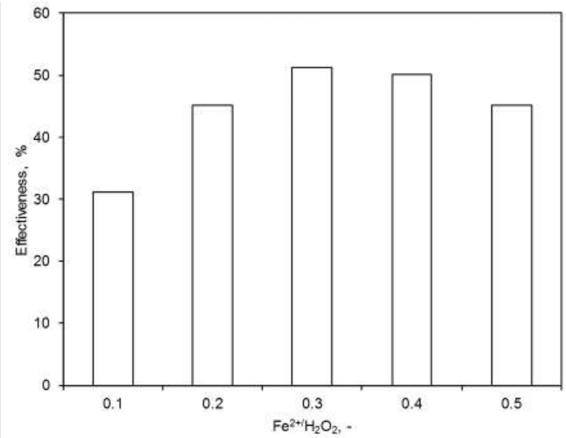

Figure 3.
Impact of Fe^{2+}/H_2O_2 mass ratio on effectiveness of decrease of COD

The highest COD reduction efficiency was obtained for the mass ratio Fe^{2+}/H_2O_2 of 0.3, which was already assumed in stages I and II. A change in the value of this parameter is therefore not required.

Fenton reaction time was determined using the reaction pH selected in stage I, i.e. pH 2.5, the dose of H_2O_2 selected in stage II, i.e. 5.00 g H_2O_2/L and the mass ratio Fe^{2+}/H_2O_2 selected in stage III, i.e. 0.3. The process efficiency was tested for these parameters using different reaction times of 45, 60, 120 and 180 min respectively. The results are shown in Fig. 4.

Also in this case, the process time of 120 min, already tested in stages I-III, turned out to be sufficient for the successful course of the Fenton reaction (effectiveness of COD reduction by approx. 51%). Shortening the process time resulted in a decrease in its effectiveness. In turn, its increase, e.g. to 180 min, only slightly improved the efficiency of the process (reduction of COD by approx. 52%).

The determined effective parameters of the Fenton process for the tested wastewater without the addition of used baths from the foundry industry were: wastewater pH 2.5, dose of hydrogen peroxide 5 g/L, mass ratio of Fe^{2+}/H_2O_2 of 0.3 and process time 120 min.

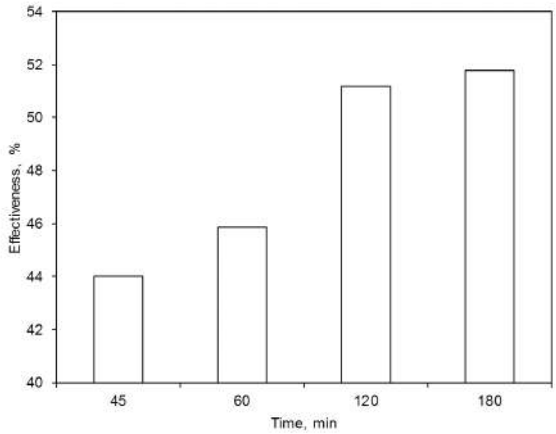

Figure 4.
Impact of time of reaction on effectiveness of decrease of COD

It should be added that as a result of the Fenton reaction, a clear increase in the concentration of chloride and sulfate ions in treated wastewater was noted. The comparison was made for a sample of wastewater before and after the treatment process with the selected process parameters (Fig. 5). This phenomenon was the result of introducing these ions into the wastewater together with the reagents included in the Fenton reagent, i.e. sulfuric (VI) acid, which was to acidify the reaction environment, and iron (II) chloride, which was the source of Fe^{2+} ions.

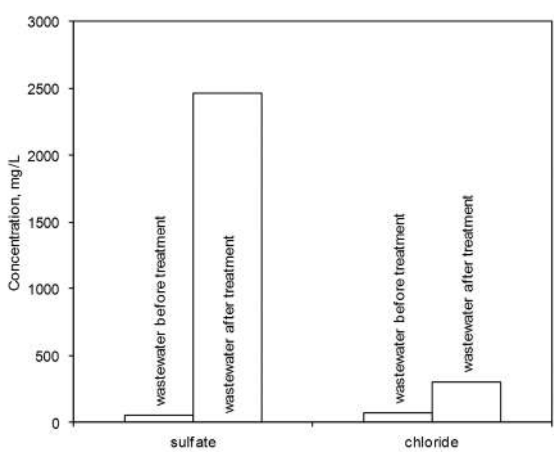

Figure 5.
The change of the concentration of sulfate and chloride ions in wastewater before and after the purification process

4. CONSLUSION

- The research showed the possibility of using the Fenton process in a multi-stage system for the treatment of real wastewater from the foundry industry. This process enables effective reduction of the concentration of organic substances measured with the COD index (approx. 51%). It also enabled a significant reduction in NS concentration (approx. 96%).
- An unfavorable phenomenon accompanying wastewater treatment in the Fenton process is the increase in salinity of wastewater after the process, including the concentration of sulfate and chloride ions. This is due to the high demand for reagents present in Fenton's reagent, including sulfuric (VI) acid and iron (II) chloride.

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